Final
Total Maximum Daily Load for pH

One Stream Segment within the
Cypress Creek Watershed
Muhlenberg County, Kentucky

May 2010

Submitted to:
United States Environmental Protection Agency
Region IV
Atlanta Federal Building
61 Forsyth Street SW
Atlanta, GA 30303-1534

Prepared by:
Kentucky Water Resources Research Institute
University of Kentucky
Lexington, KY 40506

In cooperation with:
Kentucky Department for Environmental Protection
Division of Water
200 Fair Oaks Lane
Frankfort, KY 40601

Commonwealth of Kentucky
Steven L. Beshear, Governor

Energy and Environment Cabinet
Len Peters, Secretary

Printed on recycled/ recyclable paper with state (or federal) funds.

-Final-
Total Maximum Daily Load (TMDL)

- pH (H^+ Ion Mass) -

Cypress Creek Watershed
Muhlenberg County, Kentucky

May 2010

<u>List of Contributors</u>

Dr. Lindell Ormsbee, Supervisor

Mohammad Tufail, P.E., Ben Albritton, Data Analysis and Report Preparation

Kentucky Department for Environmental Protection
Division of Water

This report is approved for release

Sandra L. Gruzesky, P.E.
Director

5/24/10
Date

Table of Contents

Figures **Page**

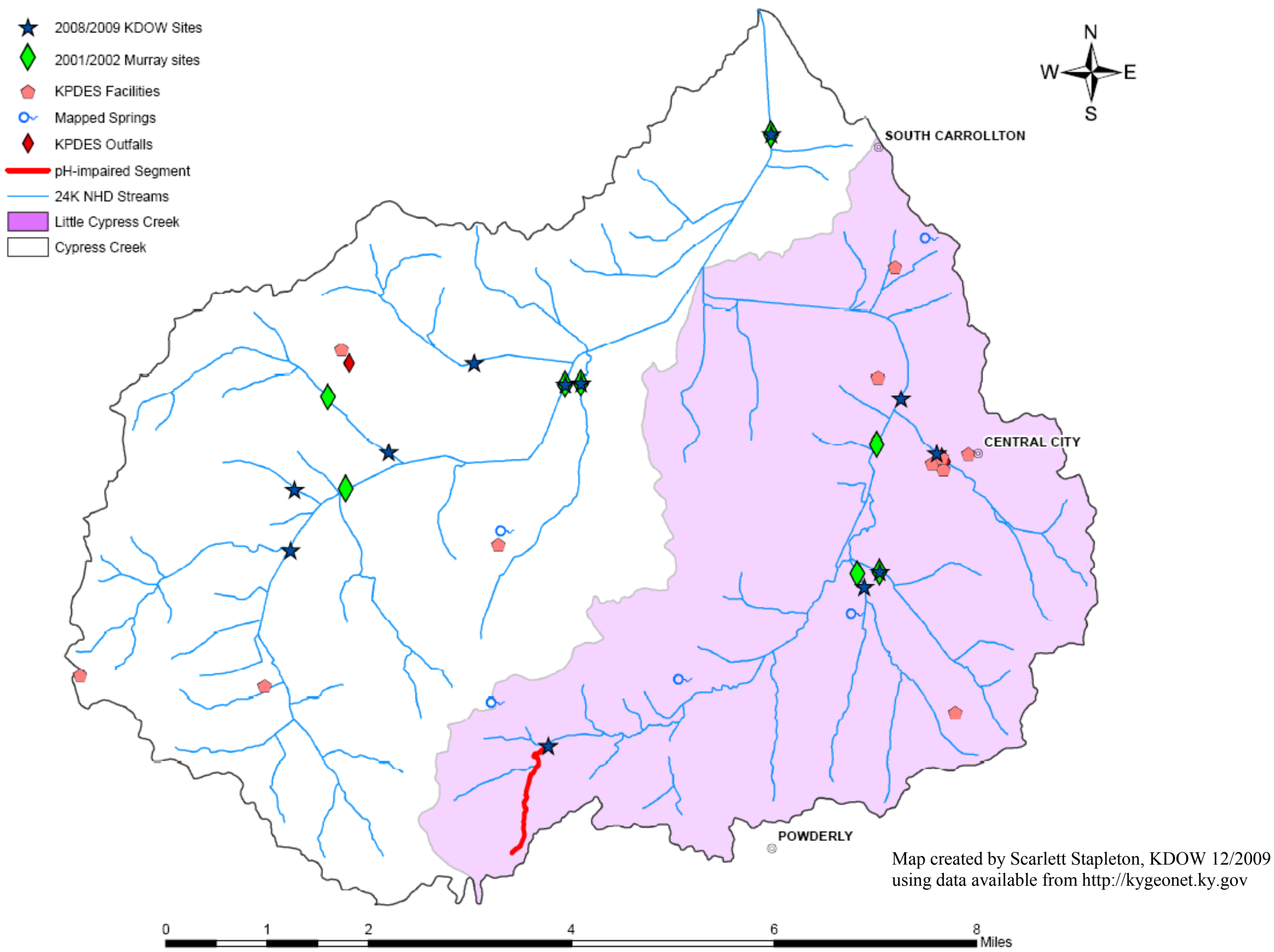
Tables **Page**

Total Maximum Daily Load (TMDL) Fact Sheet

Project Name:	Cypress Creek
Location:	Muhlenberg County, Kentucky
GNIS Number/ Waterbody ID:	KY496701_02
Scope/Size:	Cypress Creek watershed - 34,842 acres (54.44 mi^2) TMDL is for River Mile (RM) 8.7 to 10.1 in Little Cypress Creek, a tributary to Cypress Creek
Land Type:	Forest, agricultural, barren/spoil
Type of Activity:	Acid Mine Drainage (AMD) caused by Abandoned Mines
Pollutant(s):	H^+ Ion mass (pH)
TMDL Issues:	Nonpoint Sources (Abandoned Mine Lands)
Water Quality Standard/Target:	pH shall not be less than six (6.0) or more than nine (9.0) and shall not fluctuate more than one and zero-tenths (1.0) pH unit over a 24-hour period. This water quality standard (WQS) is found within 401 KAR 10:031.
Data Sources:	Kentucky Pollutant Discharge Elimination System (KPDES) Permit Historical Sampling Data, Murray State University Sampling Data, Kentucky Division of Water Sampling Data, Kentucky Division of Geographic Information Spatial Data (http://kygeonet.ky.gov)
Control Measures:	Kentucky Watershed Framework, Kentucky nonpoint source TMDL implementation plan, KPDES
Summary:	A segment in the headwaters of Little Cypress Creek was placed on the proposed 2010 303(d) list for TMDL development after it was found to not support the designated uses of primary and secondary contact recreation (PCR and SCR; swimming and wading) and warm water aquatic habitat (WAH; aquatic life). The stream segment is characterized by a depressed pH, the result of acid mine drainage from abandoned mining sites. The period of lowest pH is generally at low-flow conditions; however, the period of greatest hydrogen ion load is at higher flow conditions. The lowest mean annual flow condition in the most recent ten years was chosen as

the critical flow. Murray State was contracted to collect pH readings and corresponding stream flow measurements at eight different locations within the watershed from 2001 to 2002 (see figure below). The Kentucky Division of Water (KDOW) revisited the watershed from 2008 to 2009 collecting pH readings and flow measurements at twelve different sites.

The latest sampling indicated that previously impaired segments on the main stem of Cypress Creek were now fully supporting their PCR/SCR and WAH designated uses based upon the WQS for pH. The KDOW proposes delisting the former Cypress Creek pH impairments (RM 23.1 to 26.5 and 26.5 to 33.6) in the 2010 Integrated Report (IR). This sampling also revealed a new pH impairment in the headwaters of Little Cypress Creek. The KDOW proposes adding this stream from RM 8.7 to 10.1 to the 2010 IR as impaired for the PCR/SCR and WAH designated uses based on a 100% exceedance of pH WQS.



Monitoring Sites and pH-Impaired Segment for the Cypress Creek Watershed

TMDL Development: TMDLs in grams H^+ ions per day were computed based on the allowable minimum pH value (6.0) for waterbodies to meet PCR, SCR and WAH designated uses. The TMDL was completed for grams of ions (subsequently converted to pounds/day) since the units for pH do not allow for the computation of a quantitatively useful load or reduction amount.

In recognition of the inherent difficulties associated with imposition of a “no-exceedance” pH criteria on potentially intermittent streams, KDOW decided to use the lowest one year average discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated loading reduction. Previous pH TMDLs have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed data. The selection of the 10-year frequency was based on a consideration of water quality standards (i.e. 7Q10). However, since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of KDOW was to use the 1-year duration. The use of an average annual flow as the basis for determining the TMDL provides more appropriate mechanism for determining: (1) the total annual load; (2) the total annual reduction that would be derived from an annual summation of the daily TMDLs; and (3) the associated daily load reductions for the critical year using historical daily flows.

TMDL for Little Cypress Creek: A TMDL for pH was developed for the headwaters of Little Cypress Creek - the lowest pH condition extends along a segment from RM 8.7 to 10.1, near Site DOW03005007. The TMDL and associated load reductions are shown below.

TMDL and Associated Load Reduction in the Little Cypress Creek Watershed

Site	Upstream Contributing Area (mi2)	Critical Flow (cfs)	TMDL for a pH of 6.0 (lbs/day)	Predicted Load (lbs/day)	Load Reduction Needed (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	2.54	1.58	0.0085	13.3332	13.3247

New Permits: New permits for discharges to streams in the Cypress Creek Watershed could be allowed anywhere with the exception of the watershed area draining to the impaired segment of Little Cypress Creek. New permits in this area could be allowed contingent upon effluent pH permit limits in the range of 6.35 to 9.0 standard units. Kentucky WQS state that the pH value should not be less the 6.0 nor greater than 9.0 for meeting the designated uses of PCR/SCR and WAH. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits; however, because a stream impairment exists (low pH), new discharges cannot cause or contribute to an existing impairment. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2005). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low-pH impairment. Permits having an effluent limit pH of 6.35 to 9.0 standard units will not be assigned a hydrogen ion load as part of a Waste Load Allocation (WLA). There are currently no active permits in the headwaters of Little Cypress Creek.

Distribution of Load: Because there were no KPDES-permitted (i.e. point source) discharges to the Little Cypress Creek impaired segment during the 2008/2009 study period, the hydrogen ion load for the watershed was defined entirely as a nonpoint source load. Because new permits (pH 6.35 to 9.0) would not cause or contribute to the existing impairment, no load has been provided for the WLA category.

Wasteloads and Load Allocations in the Cypress Creek Watershed

Site	Critical Flow (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation (lbs/day)	Load Allocation (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	1.58	0.0085	0.00	0.0085

Implementation/ Remediation Strategy: Remediation of pH-impaired streams as a result of current mining operations is the responsibility of the mine operator. The Kentucky Department for Natural Resources is responsible for enforcing the Surface Mining Control and Reclamation Act of 1977 (SMCRA). The Kentucky

Division of Abandoned Mine Lands (DAML) is charged with performing reclamation to address the impacts from pre-law mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of abandoned mine land (AML) problem types.

Practical application of pH TMDLs, especially for AML, will normally involve a phased implementation approach with associated monitoring in order to insure that the implemented measures are having the desired effect. Typical remediation strategies have involved channel restoration, re-vegetation, and the use of agricultural limestone. On sites where applicable (and funding allows) passive treatment systems have been used to treat AMD including open limestone channels, vertical flow systems, limestone dosing, and constructed wetlands.

Introduction

Section 303(d) of the Clean Water Act requires states to identify waterbodies within their boundaries that have been assessed and are not currently meeting their designated uses (per 401 Kentucky Administrative Regulations (KAR) 10:026 and 10:031). States must establish a priority ranking for such waters, taking into account its intended uses and the severity of the pollutant.

States are also required to develop Total Maximum Daily Loads (TMDLs) for the pollutants that cause each waterbody to fail to meet its designated uses. The TMDL process establishes the allowable amount (i.e. "load") of pollutant a waterbody can naturally assimilate while continuing to meet the water quality criteria (WQC) for each designated use. The pollutant load must be established at a level necessary to implement the applicable WQC with seasonal variations and a margin of safety (MOS) which takes into account any lack of knowledge concerning the relationship between effluent limitations and water quality.

Location

The Cypress Creek watershed is entirely contained within Muhlenberg and McLean Counties in southwestern Kentucky. However, the section of watershed addressed in this document is contained within Muhlenberg County only (Figure 1). Muhlenberg County is bounded on the west by the Pond River and on the east by the Green River and Mud River.

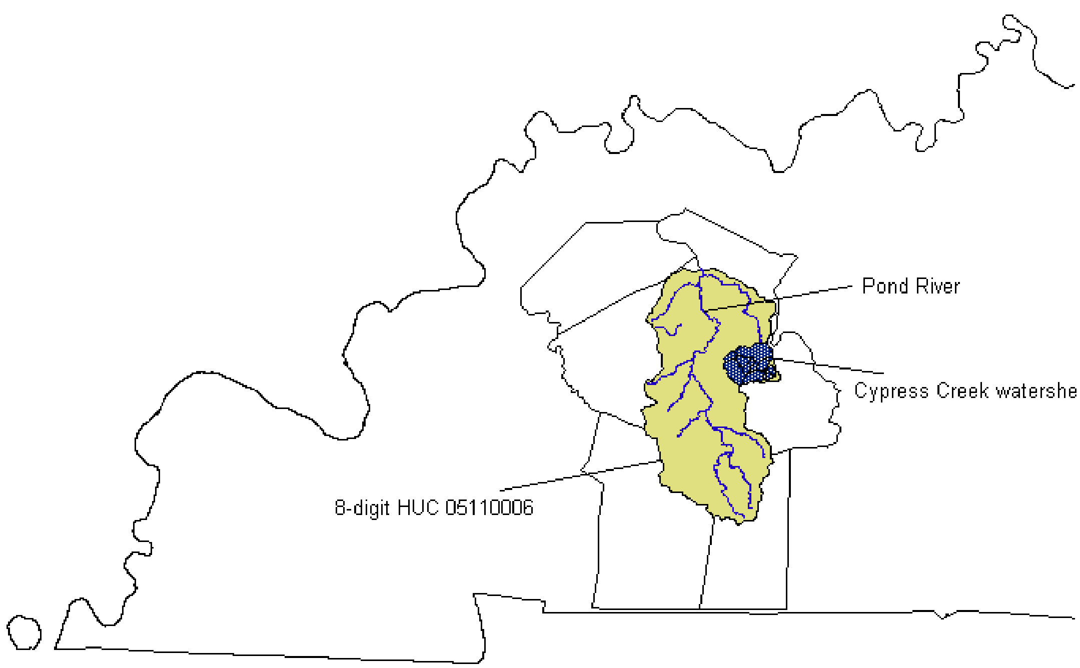


Figure 1 Location of the Cypress Creek Watershed

Hydrologic Information

Cypress Creek, a third order stream, originates in northwestern Muhlenberg County and flows north/northeast towards McLean County to discharge into Pond River, 1.06 miles upstream from its confluence with the Green River. The Green River carries the water north to the Ohio River. Cypress Creek's main stem is approximately 10.4 miles long and drains an area of 34,842 acres (54.44 mi^2). The average gradient is 5.8 feet per mile. Elevations for Cypress Creek (portion under consideration in this report) range from 450 ft above mean sea level (msl) in the headwaters to 390 ft above msl at the most downstream point.

Geologic Information

The Cypress Creek watershed is in the Western Kentucky Coal field physiographic region. The surface bedrock is of Pennsylvanian age. Formations of the Pennsylvanian age are mostly sandstone, siltstone, coal, and interbedded limestone and shale; alluvial deposits of siltstone and crossbedded sand or sandstone underlie the extensive lowland areas (US Department of Agriculture, 1977). The relief of the Cypress Creek watershed ranges from nearly level to steep. Gently sloping to steep soils are found in the uplands and nearly level soils are found on the floodplain.

Soils Information

The Cypress Creek watershed is dominated by nearly level, loamy and clayey soils near the mouth and level to steep, loamy soils in the headwaters. The major soil association found in the watershed is the Udorthents soil, which consists of strip mine spoil containing rock fragments.

Landuse Information

Coal, oil, and natural gas are among the natural resources of Muhlenberg County. Coal is the county's most important revenue-producing natural resource and at one time Muhlenberg County was the largest coal-producing county in the United States. In 1973, this county produced over 19 million tons of coal from surface strip mines and over 5 million tons from underground mines. The Cypress Creek watershed contains three main land uses: resource extraction (mining and disturbed land area), forest, and agriculture (Table 1).

Mining History

Mining activities in the Cypress Creek watershed have occurred since the 1970s. A list of the various mining permits that have been issued for Cypress Creek is provided in Table 2. Mining permits in Kentucky are classified on the basis of whether the original permit was issued prior to May 3, 1978 (pre-law permit), after January 18, 1983 (post-Kentucky primacy) or between these dates (interim period).

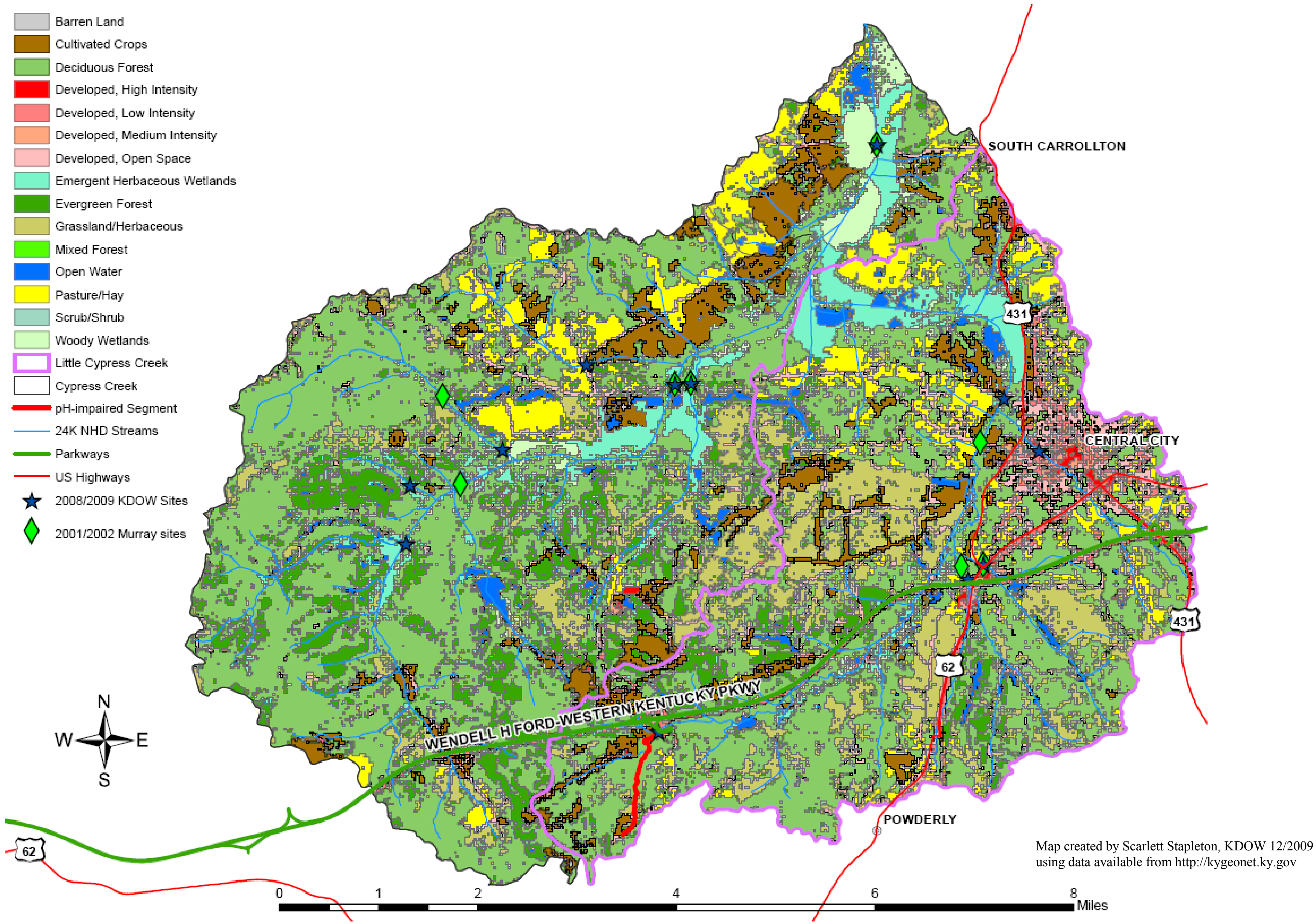


Figure 2 Land Cover in the Cypress Creek Watershed (2001 MRLC NLCD)

Table 1 Land Cover in the Cypress Creek Watershed (2001 MRLC NLCD)

Cypress Creek (excluding Little Cypress Creek)		
Land Cover	**% of Total Area**	**Acres**
Open Water	2.25%	398.88
Forest	49.40%	12,764.24
Agriculture (total)	23.20%	2,835.77
Pasture	11.65%	1,381.02
Row Crop	11.55%	1,454.75
Developed	3.31%	639.91
Natural Grassland	4.59%	1,477.51
Wetland	17.24%	1,818.17
Barren	0.08%	27.17
Little Cypress Creek		
Land Use	**% of Total Area**	**Acres**
Open Water	2.03%	319.20
Forest	49.47%	7,763.38
Agriculture (total)	14.59%	2,288.95
Pasture	8.74%	1,371.14
Row Crop	5.85%	917.80
Developed	13.86%	2,175.41
Natural Grassland	14.51%	2,277.35
Wetland	5.46%	857.52
Barren	0.14%	21.87

Table 2 History of Mining Permits in the Cypress Creek Watershed

Permit #	Permitted Area (ac)	Associated Company	Date Issued	Date Expired
8890008	1061	Peabody Coal Company	03/28/1984	02/01/1994
8890054	38	Peabody Coal Company	01/22/1990	01/22/1995
8890064	73	Peabody Coal Company	07/11/1991	07/11/1996
8890071	91.2	Hawkins/Thomson Partnership	09/24/1992	09/24/2002
8890109	27	Schoate Mining Co. LLC	01/16/2002	01/16/2007
8890113	24.7	C & R Coal Company Inc.	09/04/2001	09/04/2006
8895006	825	Peabody Coal Company	09/30/1986	09/30/1996
8895009	10029.8	Kenamerican Resources Inc.	10/17/1994	09/30/2006
8898000	625	Peabody Coal Company	08/06/1984	08/06/2004

An explanation of the permit numbering system is provided in Appendix A. All permits are secured through reclamation bonds. A reclamation bond is a financial document submitted to the Kentucky Department of Surface Mining Reclamation and Enforcement (DSMRE) prior to mine permit issuance. A bond guarantees mining and reclamation operations will be conducted by mining companies according to regulations and the terms of the approved permit. If a coal company cannot comply with these conditions, the bond is "forfeited" (paid to the DSMRE) for eventual use by the Kentucky Division of Abandoned Mine Lands (DAML) in reclaiming the mined area. Reclamation bonds may be submitted in the forms of cash, certificate of deposit, letter of credit or surety (insurance policy).

A reclamation bond may be returned to a coal company by either of two methods: administrative or phase (on-ground reclamation). Administrative releases occur when new bonds are substituted for the original bonds. Administrative releases are also given for areas of a mine site that are permitted, but never disturbed by mining or for areas that are included under a second more recently issued permit.

Phase releases occur in three stages and according to specific reclamation criteria: Phase One – all mining is complete, and backfilling, grading and initial seeding of mined areas has occurred; Phase Two – a minimum of two years of growth on vegetated areas since initial seeding, the vegetation is of sufficient thickness to prevent erosion and pollution of areas outside the mine area with mine soils, and any permanent water impoundments have met specifications for future maintenance by the landowner; and Phase Three – a minimum of five years of vegetative growth since initial seeding and the successful completion of reclamation operations in order for the mined area to support the approved postmining land use. Up to 60 percent of the original bond amount is released at Phase One. An additional 25 percent is returned at Phase Two, with the remainder of the reclamation bond released at Phase Three. Once a permit is released and the reclamation bond returned, the state cannot require additional remediation action by the mining company unless it is determined that fraudulent documentation was submitted as part of the remediation process.

Monitoring History

The waters of Cypress Creek were monitored as early as 1978 by the Kentucky Division of Water (KDOW) as reported in *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky*, published in 1981 by KDOW as part of an agreement with DAML. The KDOW recorded a pH value of 4.6 at the outlet of the watershed (i.e. near Site 1) on April 28, 1978.

Additional monitoring was performed in the Cypress Creek watershed as permits were granted to mining companies. Several sampling stations were established to monitor the water quality characteristics of the tributaries and main stem of Cypress Creek in association with two mining permits. A summary of the historic pH readings at these sites are shown in Table 3. A few of the readings were below a pH value of 6.0.

Based on this information, two segments of Cypress Creek were placed on the 1996 and subsequent 303(d) lists for partial support of the warm water aquatic habitat (WAH) and primary and secondary contact recreation (PCR/SCR; swimming and wading) designated uses due to low pH from acid mine drainage (AMD).

Table 3 Historic Monitoring Stations and pH Data

Station		Date	pH
Latitude	Longitude		
37-15-4	87-14-29	4/28/1978	5.2
37-15-48	87-14-55	4/28/1978	5.3
37-17-29	87-12-39	4/28/1978	6.9
37-18-10	87-11-50	4/28/1978	7.3
37-20-20	87-9-40	4/28/1978	7.4
37-59-59	87-15-5	11/20/1978	5.0
37-26-45	87-11-52	4/13/1978	7.1
37-28-31	87-13-31	4/13/1978	7.2
37-29-25	87-14-43	4/12/1978	7.0
37-29-20	87-17-10	4/12/1978	7.0
37-30-32	87-19-0	4/12/1978	6.9

Reclamation History

No reclamation history was found for the Cypress Creek watershed. However reclamation activities are underway at other locations within the State where water quality is affected by AMD. From 1985 through 2008, the DAML has spent approximately $24.5 million dollars on various reclamation projects in western Kentucky.

Problem Definition

TMDL monitoring conducted by KDOW from 2008 to 2009 indicated that the formerly impaired segments of Cypress Creek are now fully supporting their PCR/SCR and WAH designated uses based upon the WQC for pH, however new pH impairment was found in the headwaters of Little Cypress Creek. The delisting of the Cypress Creek pH impaired segments and listing of the new Little Cypress Creek (from RM 8.7 to 10.1) pH impaired segment are both proposed in the 2010 Integrated Report to Congress.

The Cypress Creek watershed provides an example of impairment caused by AMD. Bituminous coal mine drainage, like that found in the Cypress Creek watershed, may contain very concentrated sulfuric acid and high concentrations of metals, especially iron, manganese, and aluminum. AMD can; (1) ruin domestic and industrial water supplies; (2) decimate aquatic life; and (3) cause waters to be unsuitable for swimming and wading. In addition to these problems, a depressed pH interferes with the natural stream self-purification processes. At low pH levels, the iron associated with AMD is soluble. However, in downstream reaches where the pH begins to rise, most of the ferric sulfate [$Fe_2(SO_4)_3$] is hydrolyzed to essentially insoluble iron hydroxide [$Fe(OH)_3$]. The stream bottom can become covered with a sterile orange or yellow-brown iron hydroxide deposit that impacts benthic algae, invertebrates, and fish.

The sulfuric acid in AMD is formed by the oxidation of sulfur contained in the coal and/or the rock or clay found above and below the coal seams. Most of the sulfur in the unexposed coal is found in a pyritic form as iron pyrite and marcasite (both having the chemical composition FeS_2).

In the process of mining, the iron sulfide (FeS_2) is uncovered and exposed to the oxidizing action of oxygen in the air (O_2), water, and sulfur-oxidizing bacteria. The end products of the reaction are as follows:

$$4\ FeS_2 + 14\ O_2 + 4\ H_20 + \text{bacteria} \rightarrow 4\ Fe + SO_4 + 4\ H_2SO_4 \qquad (1)$$

The subsequent oxidation of ferrous iron and acid solution to ferric iron is generally slow. The reaction may be represented as:

$$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \qquad (2)$$

As the ferric acid solution is further diluted and neutralized in a receiving stream and the pH rises, the ferric iron [Fe^{3+} or $Fe_2(SO_4)_3$] hydrolyzes and ferric hydroxide [$Fe(OH)_3$] may precipitate according to the reaction:

$$2\ Fe_2(SO_4)_3 + 12\ H_2O \rightarrow 4\ Fe(OH)_3 + 6\ H_2SO_4 \qquad (3)$$

The brownish yellow ferric hydroxide ($Fe(OH)_3$) may remain suspended in the stream even when it is no longer acidic. Although the brownish, yellow staining of the stream-banks and water does not cause the low pH, it does indicate that there has been production of sulfuric acid. The overall stoichiometric relationship is shown in equation (4):

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \longleftrightarrow 8\ H_2SO_4 + 4\ Fe(OH)_3 \qquad (4)$$

This reaction (eqn. 4) indicates that a net of 4 moles of H+ are liberated for each mole of pyrite (FeS_2) oxidized, making this one of the most acidic weathering reactions known.

Target Identification

The endpoint or goal of a pH TMDL is to achieve a pH concentration and associated hydrogen ion load in lbs/day that supports aquatic life and recreation uses. The pH criterion to protect these uses is in the range of 6.0 to 9.0 standard units (see 401 KAR 10:031). For a watershed impacted by AMD, the focus will be on meeting the lower criterion. WQC have not been specified in terms of a particular frequency of occurrence. As pointed out in the 2001 National Research Council report, *Assessing the TMDL Approach to Water Quality Management (NRC, 2001)*, "All chemical criteria should be defined in terms of magnitude, frequency, and duration." Each of these three components is pollutant-specific and may vary with season. The frequency component should be expressed in terms of a number of allowed flow excursions in a specified period (return period) and not in terms of the low flow or an absolute "never to be exceeded" limit.

Water quality criteria may occasionally be exceeded because of the variability of natural systems and discharges from Kentucky Pollutant Discharge Elimination System (KPDES) permitted and non-KPDES permitted sources. Small intermittent streams are especially vulnerable to this variability.

The Technical Support Document for Water Quality-Based Toxic Control (EPA, 1991) states that daily receiving water concentrations (loads) can be ranked from the lowest to the highest without regard to time sequence. In the absence of continuous monitoring, such values can be obtained through continuous simulation or Monte-Carlo analysis. A probability plot can be constructed from these ranked values, and the frequency of occurrence of any 1-day concentration of interest can be determined. Where the frequency (or probability) of the resulting concentration is greater than the maximum exceedance frequency of the water quality standard (WQS) (e.g. once in 10 years), associated load reductions will be required until the resulting concentration is above the minimum target value (e.g. pH = 7.0). Where the load and the associated target value can be directly related through a flow rate (also referred to as discharge or streamflow), the frequency (or probability) of the associated flow rate (e.g. 365Q10) can be directly related to the frequency (or probability) of the target pH.

In recognition of the inherent difficulties associated with imposition of a "no-exceedance" pH criteria on potentially intermittent streams, KDOW decided to use the lowest one year average daily discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated load reduction. Previous pH TMDLs have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed data. The selection of the 10-year frequency was based on a consideration of water quality standards (i.e. 7Q10). However since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of the KDOW was to use the 1-year duration. Use of an average daily flow over a one year period as the basis for determining the TMDL provides an appropriate mechanism for determining: (1) the total annual load; (2) the total annual reduction that would be derived from an annual summation of both the daily TMDLs; and (3) the associated daily load reductions for the critical year using the actual historical daily flows. The equivalent total annual load can be determined by simply multiplying the TMDL (derived by using the average daily flow) by 365 days. Likewise, the equivalent total annual load reduction can be obtained by multiplying the average daily load reduction (derived by using the average daily flow over a one year period) by 365 days. Although the 10-year average lowest daily flow (which roughly corresponds to the 365Q10) is typically only exceeded by approximately 20% of the days in the critical year, it still provides for explicit load reductions for approximately 80% of the total annual flow. For actual daily flows less than average flow, incremental load reductions may be accomplished by explicit imposition of a pH standard of 6.0 standard units.

Source Assessment

Permitted Sources

Permitted sources include all sources regulated by the KPDES permitting program. The KPDES program regulates both point sources and storm water discharges such as those regulated under the Municipal Separate Storm Sewer System (MS4) program. According to 401 KAR 10:002, a point source is "any discernable, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, or concentrated animal feeding operation [CAFO], from which pollutants are or may be discharged. The term does not include agricultural and stormwater run-off or return flows from irrigated agriculture." KPDES is not the only permitting program for sources that may discharge to surface water within a watershed, or otherwise affect water quality or quantity. Other permitting examples include water withdrawal permits, permits to build structures within a floodplain and permits to land apply waste from sewage treatment plants. However, within the framework of the TMDL process a KPDES permitted (i.e. point) source is defined as one regulated under the KPDES program

There are several active KPDES permitted sources in the Cypress Creek watershed however none of them discharge to the pH-impaired segment – these sources are further discussed in the 'Permitting' section of the document.

Non-Permitted Sources

Non-permitted sources include all sources not permitted by the KPDES permitting program, and are often referred to as nonpoint sources. According to 401 KAR 10:002, nonpoint means "any source of pollutants not defined as a point source, as used in this chapter." While KPDES permits are not required for non-permitted sources, their loads to surface water are still regulated by laws such as the Kentucky Agricultural Water Quality Act (i.e., implementation of individual agriculture water quality plans and corrective measures), the federal Clean Water Act (i.e., the TMDL process) and 401 KAR 10:037 (Groundwater Protection Plans), among others. Nonpoint (non KPDES-permitted) sources of pollution are often associated with land use. Many of the mining permits discussed in *Mining History* (and Table 2) are associated with AML and AMD (i.e. pre-SMCRA permits not associated with the KPDES). Pollutant loading associated with AML is thus classified as a nonpoint source load.

Previous monitoring has been performed in the Cypress Creek watershed in conjunction with mining permits. The historic pH readings at these sites (Table 3) indicate impairment due to low pH in the western portions of watershed.

2001-2002 Sampling

In order to provide a more recent characterization of the pH levels in the watershed, the University of Kentucky contracted with Murray State University to collect additional data from the watershed. A summary of the results obtained from these sites is shown in

Table 4 with their locations depicted in Figure 3. The sampling indicated pH degradation in the lower portion of the watershed near site 1 confirming the downstream segment's pH impairment. With the exception of single observations at sites 2 and 3, all sample results at the other sites yielded pH values greater than 6.0 standard units.

2008-2009 Sampling

The KDOW TMDL Section revisited the Cypress Creek watershed from 2008 to 2009. Parameters collected included pH and stream flow measurements at twelve different sites across the watershed (Table 5 and Figure 3). This sampling indicated that the previously impaired segments are now fully supporting their PCR/SCR and WAH designated uses based upon the WQC for pH. The KDOW proposes delisting the former Cypress Creek pH impairments (RM 23.1 to 26.5 and 26.5 to 33.6) in the proposed 2010 IR. The KDOW sampling also revealed a new pH impairment in the headwaters of Little Cypress Creek; the KDOW proposes adding this stream from RM 8.7 to 10.1 to the proposed 2010 IR as impaired for the PCR/SCR and WAH designated uses based on a 100% exceedance of the pH water quality criterion.

Table 4 2001/2002 Murray State University Sample Results

Date	Site 1 37-20-36 N 87-09-68 W		Site 2 37-18-05 N 87-14-42 W		Site 3 37-16-78 N 87-14-74 W		Site 4 37-18-28 N 87-11-31 W		Site 5 37-18-21 N 87-11-67 W	
	Flow rate (cfs)	pH	Flow rate (cfs)	pH	Flow rate (cfs)	pH	Flow rate (cfs)	pH	Flow rate (cfs)	pH
9/8/01	35	**5.6**	0.2	6.3	2	6.3	7	6.6	4	6.5
9/22/01	64	**5.5**	0.4	6.2	2	6.5	7	6.6	4	6.5
11/3/01	39	**5.5**	0.0	6.3	4	6.2	8	6.7	4	6.9
11/17/01	39	**5.7**	1.0	**5.7**	2	7.4	8	6.7	4	6.6
12/1/01	2064	**5.8**	7.0	6.1	40	**5.4**	195	6.4	77	6.4
1/26/02	685	6.8	3.0	7.7	13	6.4	61	7.2	5	7.1
2/23/02	69	6.9	2.0	7.5	9	6.7	16	7.3	4	7.6
4/6/02	61	7.0	3.0	7.3	16	6.7	19	7.3	4	7.5
4/20/02	202	6.6	2.0	7.2	12	6.3	21	6.9	4	7.1
5/4/02	340	6.2	2.0	7.3	18	6.2	21	6.6	4	6.9

Date	Site 8 37-17-72 N 87-08-46 W		Site 9 37-16-36 N 87-08-23 W		Site 11 37-16-27 N 87-08-35 W	
	Flow rate (cfs)	pH	Flow rate (cfs)	pH	Flow rate (cfs)	pH
9/8/01	9	6.5	2	7.0	4	7.0
9/22/01	8	7.3	2	7.6	3	7.6
11/3/01	10	7.0	2	7.4	4	7.5
11/17/01	5	6.6	2	7.2	5	7.5
12/1/01	129	6.7	7	6.9	10	6.8
1/26/02	73	6.7	3	7.4	10	7.3
2/23/02	14	7.6	5	7.7	6	7.7
4/6/02	22	7.6	3	7.8	5	7.7
4/20/02	60	7.3	3	7.6	5	7.6
5/4/02	60	6.8	3	7.2	11	7.3

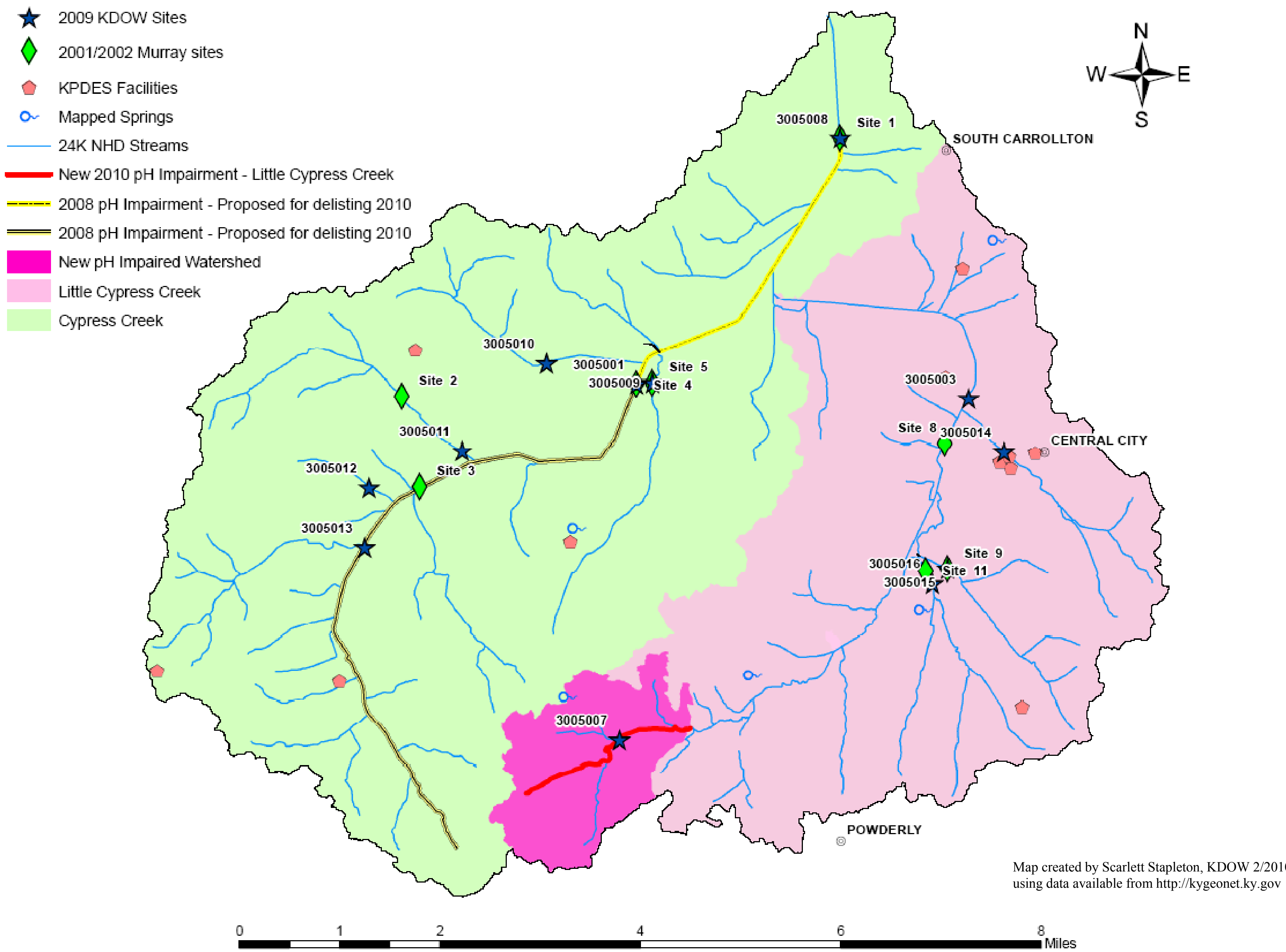


Figure 3 Sampling Sites in the Cypress Creek Watershed Monitored by Murray and KDOW

Table 5 2008/2009 KDOW Sample Results

DOW03005001			DOW03005003			DOW03005007			DOW03005008			DOW03005009			DOW03005010		
Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow
11/18/08	7.18	**	11/18/08	6.88	18.986	11/18/08	**2.37**	0.239	5/12/09	6.54	**	5/12/09	6.82	**	5/12/09	7.13	**
12/11/08	7.07	77.580	1/7/09	7.65	**	1/7/09	**4.51**	N/A	5/26/09	6.87	**	5/26/09	6.96	**	5/26/09	7.30	**
1/8/09	7.19	**	2/17/09	6.71	**	3/26/09	**3.03**	2.186	6/9/09	6.85	**	6/9/09	6.99	**	6/9/09	7.31	**
2/17/09	6.86	**	3/26/09	7.03	**	4/22/09	**2.82**	2.423	6/23/09	6.73	**	6/23/09	6.80	**	6/23/09	7.09	**
3/26/09	7.22	**	4/21/09	7.08	**	5/13/09	**2.48**	1.595	7/8/09	6.99	**	7/7/09	6.78	**	7/7/09	6.96	**
4/21/09	7.36	**	5/12/09	6.61	**	5/27/09	**2.46**	0.837	7/24/09	6.57	**	7/24/09	6.59	**	7/23/09	7.15	**
5/12/09	6.75	**	5/26/09	6.86	**	6/10/09	**2.95**	0.950	8/31/09	6.96	**	8/4/09	7.12	**	8/4/09	7.48	**
5/26/09	6.91	**	6/9/09	7.06	**	6/23/09	**3.20**	1.146	9/8/09	6.85	**	8/31/09	6.97	**	8/31/09	6.99	**
6/9/09	7.14	**	6/23/09	6.76	**	7/8/09	**2.64**	0.558	9/23/09	6.78	**	9/8/09	7.00	**	9/8/09	6.94	**
6/23/09	6.94	**	7/7/09	7.07	**	7/23/09	**3.44**	2.290	10/8/09	6.90	**	9/23/09	7.03	**	9/23/09	6.86	**
7/7/09	7.00	**	7/24/09	6.63	**	8/31/09	**2.20**	0.367	10/27/09	6.60	**	10/8/09	7.09	**	10/8/09	6.91	**
7/23/09	6.76	**	8/4/09	7.15	**	9/23/09	**4.59**	**				10/27/09	7.07	**	10/27/09	6.95	**
8/4/09	7.26	**	8/31/09	7.26	**	10/27/09	**3.09**	**									
8/31/09	7.50	**	9/23/09	6.91	**												
9/8/09	6.98	**	10/8/09	6.83	**												
9/23/09	6.89	**	10/27/09	7.05	**												
10/8/09	6.75	**															
10/27/09	7.03	**															

DOW03005011			DOW03005012			DOW03005013			DOW03005014			DOW03005015			DOW03005016		
Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow	Date	pH	Flow
1/8/09	7.43	N/A	11/19/08	7.11	1.164	12/10/08	7.58	**	11/18/08	7.12	0.558	11/18/08	7.06	0.569	11/18/08	7.14	**
4/22/09	7.18	6.725	1/8/09	7.25	N/A	2/18/09	6.35	1.542	1/7/09	7.85	4.770	1/7/09	7.88	5.972	1/7/09	7.53	**
5/13/09	7.12	3.629	3/26/09	7.05	2.218	4/22/09	6.48	2.768	2/17/09	6.86	2.047	2/17/09	6.99	1.871	2/17/09	6.83	**
5/27/09	7.26	1.499	4/21/09	7.07	3.224	5/27/09	6.45	**	3/26/09	7.26	2.605	3/26/09	7.14	1.961	3/26/09	7.20	**
6/10/09	7.56	1.786	5/13/09	6.85	3.079	6/10/09	6.78	3.327	4/21/09	7.37	4.723	4/21/09	7.31	3.882	4/21/09	7.39	**
6/23/09	7.61	1.935	5/27/09	6.74	**	6/23/09	6.89	14.548	5/12/09	6.82	2.442	5/12/09	6.96	1.395	5/12/09	6.77	**
7/8/09	7.90	1.382	6/10/09	7.12	1.383	7/8/09	6.82	5.579	5/26/09	7.33	1.585	5/27/09	6.86	1.052	5/27/09	6.60	**
7/23/09	7.19	4.119	6/23/09	6.91	2.569	7/23/09	6.76	**	6/9/09	7.25	0.951	6/10/09	7.54	0.666	6/10/09	7.50	**
8/31/09	7.67	0.046	7/8/09	7.04	1.311	8/31/09	6.79	2.101	6/23/09	6.94	3.538	6/23/09	7.13	**	6/23/09	6.80	**
9/8/09	7.80	0.477	7/23/09	6.94	**	9/8/09	6.70	7.041	7/7/09	7.30	1.154	7/8/09	7.27	0.863	7/23/09	6.66	**
			7/23/09	N/A	N/A				7/23/09	6.96	**	7/23/09	6.88	**	9/8/09	7.40	**
			8/31/09	7.03	**				8/4/09	7.38	**	8/4/09	7.22	**	9/23/09	7.24	**
			9/8/09	7.12	**				8/31/09	7.55	0.626	8/31/09	7.31	**	10/8/09	7.49	**
			10/8/09	7.19	**				9/8/09	7.52	0.874	9/8/09	7.40	**	10/27/09	7.48	**
									9/23/09	7.20	**	9/23/09	7.27	**			
									10/8/09	7.20	**	10/8/09	7.15	0.881			
									10/27/09	7.32	**	10/27/09	7.16	**			

Model Development

The magnitude of the associated hydrogen ion load in a water column (in terms of activity) can be determined by measuring the pH of the water. The relation between hydrogen load and pH can be expressed as follows:

$$\{H_3O^+\} = 10^{-pH} \quad \text{or more commonly} \quad \{H^+\} = 10^{-pH} \quad (5)$$

where pH is the negative log of the H^+ ion activity in mol/L. To convert between the measured activity $\{H^+\}$ and the actual molar concentration $[H^+]$, the activity is divided by an activity coefficient, γ.

$$[H^+] = \{H^+\}/\gamma \quad (6)$$

The activity coefficient γ is dependent upon the ionic strength μ of the source water under consideration. The ionic strength of a given source water can be approximated by estimating the TDS (total dissolved solids in mg/liter or ppm) and applying the following relationship (Snoeyink and Jenkins, 1980):

$$\mu = (2.5 * 10^{-5}) * TDS \quad (7)$$

Alternatively, the ionic strength of a given source of water may be related to the measured specific conductance (SC) through the following relationship (Snoeyink and Jenkins, 1980):

$$\mu = (1.6 * 10^{-5}) * SC \quad (8)$$

Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 4 (Snoeyink and Jenkins, 1980).

In the absence of actual measured values of TDS or SC, an estimate of the upper limit of the ionic strength may be obtained from an evaluation of historic values of TDS or SC collected in the area. For example, an evaluation of over 1600 measurements of SC obtained from streams in the western Kentucky coal fields (Grubb and Ryder, 1972; KDOW, 1981; and US Geological Survey, 1983) revealed a range of values from 45 μS/cm to 5920 μS/cm. Use of an upper limit of 6000 μS/cm yields an ionic strength of 0.096 or approximately 0.10. Use of a value of ionic strength of 0.10 yields an activity coefficient of approximately 0.83.

For the Cypress Creek watershed, SC values were observed to vary from 80 to 2050 μ ohms/cm, which yields ionic strength values of 0.001 to 0.033 respectively. Application of Figure 4 for the observed ionic strengths in Cypress Creek yields activity coefficients of approximately 0.97 to 0.87.

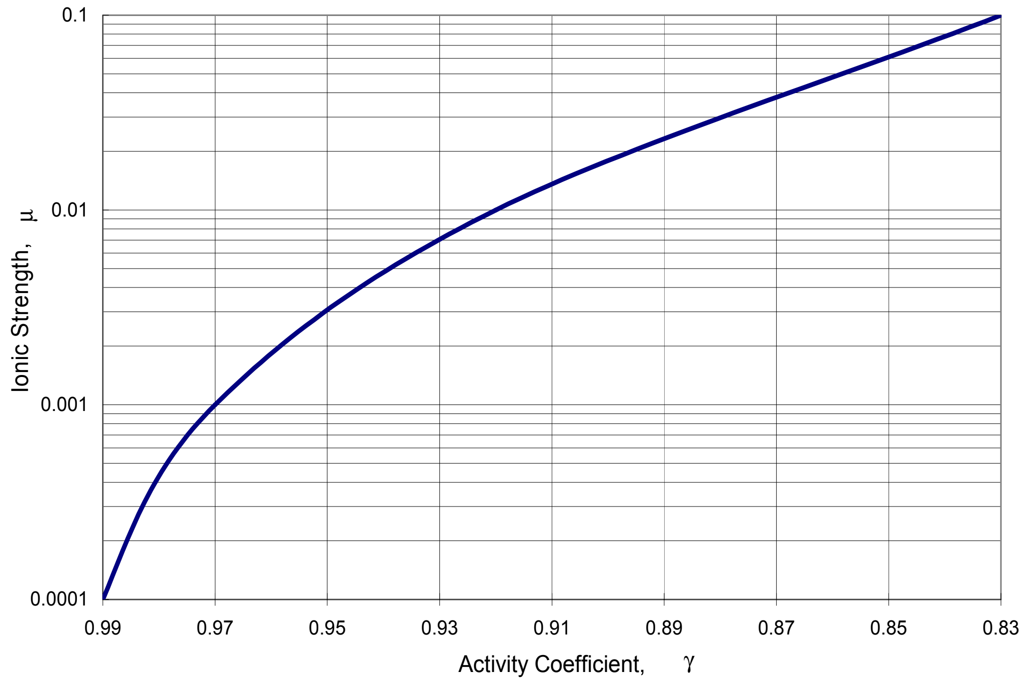


Figure 4 Activity Coefficients of H+ as a Function of Ionic Strength (Snoeyink and Jenkins, 1980)

The atomic weight of hydrogen is one gram per mole. Thus, the concentration of hydrogen ions in mol/L is also the concentration in g/L. Multiplying the concentration of hydrogen ions by the average flow rate for a given day results in a hydrogen ion load for that day in grams/day. As a result, for any given flow rate there is a maximum ion load that the stream can assimilate before a minimum pH value of 6.0 is violated. Thus, for any given day, a TMDL may be calculated for that day using the average daily flow and a minimum pH standard of 6.0 standard units.

Because pH and the equivalent hydrogen ion load can be related as a function of flow (or flow rate) and ionic strength, a functional relation can be developed between flow and the associated ion loading for a given pH value. By specifying a minimum pH value (e.g. 6) and an associated minimum activity correction factor (e.g. 0.87), an envelope of maximum hydrogen ion loads that could still yield a pH of 6 may be obtained as a function of flow (see the upper $TMDL_x$ curve in Figure 5). However, in the case of developing a TMDL for an impaired stream, the most conservative approach would be to assume an activity coefficient of 1.0, which would yield the lowest value for the TMDL for a given range of activity coefficients (see lower $TMDL_1$ curve in Figure 5). The difference between the maximum $TMDL_x$ (based on the observed activity coefficient) and the minimum $TMDL_1$ (based on an activity coefficient of 1.0) would provide a margin of safety (MOS) in setting the TMDL for the stream as well as for calculating the associated load reduction. In developing a TMDL for the Little Cypress Creek watershed, the TMDL was established assuming an activity coefficient of 1.0, while the observed load was determined using an activity coefficient of 0.87, providing for an upper limit for a MOS of approximately 13 percent. Even though this MOS can be deemed as an explicit MOS, for this TMDL it will be expressed as an implicit MOS because a conservative assumption has been used to determine the value of the TMDL.

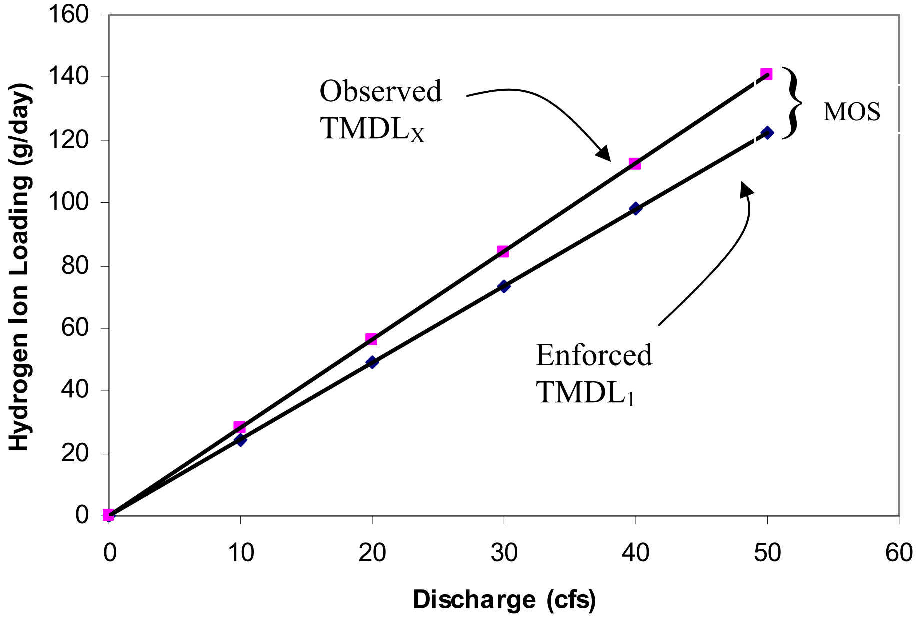


Figure 5 Relationship between Flow (Discharge) and Maximum Ion Loading for a pH of 6.0 Standard Units

Hydrogen Loading Example Calculation

In order to demonstrate the hydrogen loading conversion procedure, use the following monitoring data:

- Critical discharge (Q) = 1.58 cfs (Site DOW03005007, Little Cypress Creek)
- Measured pH = 6.0

The pH can be converted to a mole/liter measurement (i.e. moles $[H^+]$/liter) by applying the following relationship:

$$pH = -\log \{H^+\}$$

The resulting moles of hydrogen ions is the anti-log of -6.0, which is 0.000001 moles/liter. The units need to be converted into grams/cubic ft. This is accomplished by applying the following conversion factors:

- There is one gram per mole of hydrogen.
- 1 liter = 0.035314667 cubic feet

(0.000001 moles/liter)*(1 gram/mole)*(1liter/0.035314667 ft^3) = 0.0000283168 g/ft^3
The goal is to achieve a loading rate in terms of g/day, or lbs/day. If the amount of hydrogen in grams/cubic foot is multiplied by the given flow rate in cubic feet/second and a conversion factor of 86,400 s/day, then the load is computed as:

(0.0000283168 g/ft^3)*(1.58 ft^3/s)*(86400s/1day) = 3.87 g/day, or 0.0085 lbs/day

Assuming an activity correction factor of 0.87, the maximum load is 95.08 g/day, or 0.2092 lbs/day:

82.72 g/day / 0.87 = 4.45 g/day, or 0.0098 lbs/day

Thus, by using an activity coefficient of 1.0 instead of 0.87, a MOS of approximately 13 percent is realized.

TMDL Development

Theory

The TMDL is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating WQSs - it also includes a MOS. The units of a load measurement are mass of pollutant per unit time (mg/hr, lbs/day). In the case of pH there is no associated mass unit (pH is measured in Standard Units).

The TMDL is comprised of the sum of individual wasteload allocations (WLAs) for KPDES permitted sources and load allocations (LAs) for both non-KPDES permitted sources and natural background levels for a given watershed. The sum of these components may not result in exceedance of WQSs for that watershed. In addition, the TMDL must include a MOS, which is either implicit or explicit, that accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$\text{TMDL} = \text{Sum (WLAs)} + \text{Sum (LAs)} + \text{MOS} \qquad (9)$$

Margin of Safety

The MOS is part of the TMDL development process (Section 303(d)(1)(C) of the Clean Water Act). There are two basic methods for incorporating the MOS (EPA, 1991):

1) Implicitly incorporate the MOS using conservative model assumptions to develop allocations, or

2) Explicitly specify a portion of the total TMDL as the MOS using the remainder for allocations.

In using the proposed methodology, the MOS may be incorporated explicitly through the properties of water chemistry that determine the relationship between pH and hydrogen ion concentration. In an electrically neutral solution, the activity coefficient (γ in eqn. 6) is assumed to be equal to 1.0, meaning that there is no quantitative difference between activity and molar concentration. In the case of AMD, there obviously exists the possibility of additional ions in the water column that may affect the relationship between the measured activity and the associated ion load. SC values in Cypress Creek have been found to range from 80 – 2050 μS/cm (microSeimens per cm) which yield ionic strength values of between 0.001 and 0.033 respectively. Application of Figure 4 for the observed ionic strengths in Cypress Creek yields activity coefficients of approximately 0.97 – 0.87. In developing a pH TMDL for Little Cypress Creek, a conservative activity coefficient of 1.0 was assumed, while an activity coefficient of 0.87 was used in calculating the actual load, thus providing for a MOS of approximately 13 percent. Even though this MOS can be deemed as an explicit MOS, for this TMDL it will be expressed as an implicit MOS because a conservative assumption has been used in the model to determine the value of the TMDL.

TMDL Determination

Because maximum hydrogen ion loading values can be directly related to flow (Figure 5), the associated allowable ion loading can be directly related to the flow. In order to find the lowest 10-year average annual flow for the Cypress Creek watershed, a regional hydrologic frequency analysis was used. Regional analysis can be used to develop an inductive model using data collected at streamflow gauging stations that are located in the same hydrologic region as the watershed of interest. For this study, the following USGS gauging stations were selected: 03320500, 03384000, 03383000, and 03321350. The data from these gages were used to estimate the lowest average annual flows of the most recent 10 years (see Table 6). This flow was then regressed with watershed area to produce Figure 6. Using this figure, the lowest 10-year mean annual discharge for a given watershed area can be determined.

Table 6 Lowest Average Annual Flow Rates (cfs) for Stations in Regional Analysis

	USGS Gauging Station Numbers			
Station	3384000	3321350	3320500	3383000
Area (mi^2)	2.10	58.20	194.00	255.00
Q (cfs)	0.69	49.10	99.70	166.00

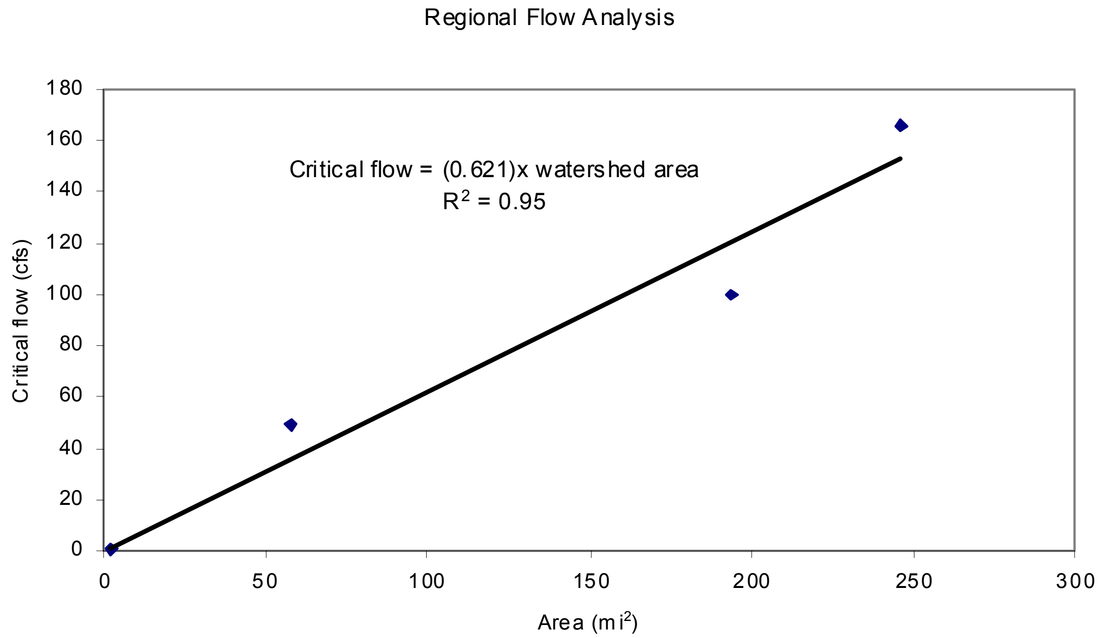


Figure 6 Relationship between Basin Area and the Critical TMDL Flow

Application of Figure 6 for the Little Cypress Creek watershed yields a TMDL critical average annual discharge of 1.58 cfs at Site DOW03005007 assuming an upstream watershed area of 2.54 mi^2. Application of a critical discharge (the lowest 10-year mean annual flow) of 1.58 cfs with the lower $TMDL_1$ curve in Figure 5 yields a cumulative TMDL for Site DOW03005007 of 0.0085 lbs/day (Table 7).

Table 7 Flows and Corresponding TMDLs

Site	Upstream Area (mi^2)	Critical Average Annual Flow (cfs)	TMDL – H+ Ion Load (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	2.54	1.58	0.0085

Hydrogen Ion Loading Model

There are currently no KPDES-permitted sources in this watershed that may contribute to the pH impairment in Little Cypress Creek. As a result, the waste load allocation for the watershed was set to zero. The entire hydrogen ion load can be attributed to nonpoint sources - for this watershed, the source is abandoned mine lands (AMLs).

Based on a physical inspection, it is hypothesized that the lowering of the pH in the stream is directly related to oxidation of sulfur that occurs as runoff flows over or through the spoil areas associated with previous mining activities (surface and underground) in the basin. Using the 2008/2009 KDOW data, an inductive model was developed at Site DOW03005007 that relates total hydrogen ion loading to flow. This model is shown in Figure 7 and is derived from data in Table 5 - data was excluded if no flow was recorded.

In developing the model, a conservative value of 0.87 was assumed for the activity coefficient based on the upper limit of measured SC values of 2050 µS/cm. A plot of the minimum TMDL curve, as shown previously in Figure 5, is also included with the model. As discussed, this curve was developed assuming an activity coefficient of 1.0, thus providing for an upper limit for a MOS for the TMDL of approximately 13 percent. These two curves thus provide a mechanism for determining the TMDL and the required load reduction for an associated critical flow. In those cases where the load model lies beneath the TMDL curve, no load reduction will be necessary.

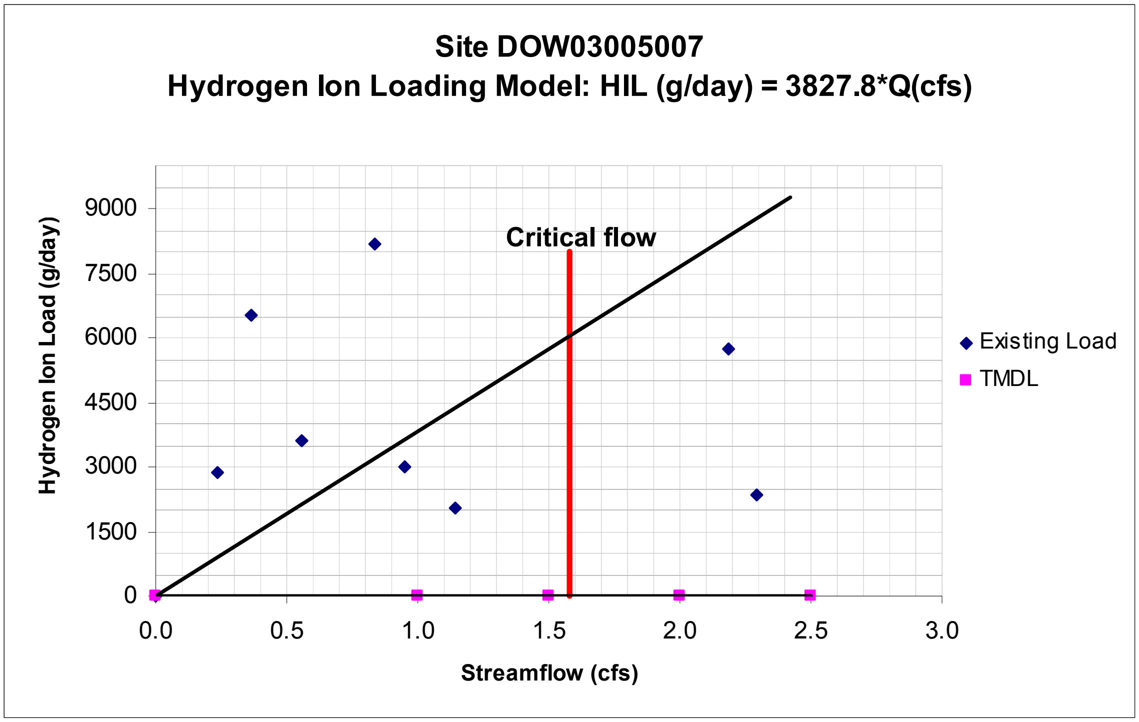


Figure 7 Relationship between Flow and Ion Load for Site DOW03005007 using 2008/2009 Monitoring Data

Predicted Load

The predicted (or existing) hydrogen ion load at Site DOW03005007 may be obtained using the critical flow from Table 5 and the associated load relation shown in Figure 7. Use of a critical flow of 1.58 cfs with the fitted line in Figure 7 yields a cumulative load of 6,047.92 g/day or 13.3332 lbs/day at site DOW 03005007 based on 2008/2009 data.

Incremental loads were calculated for all of the Murray sites using the 2001/2002 data. The hydrogen ion loading models and predicted ion loads are included as Appendix B.

Because the more recent KDOW data demonstrated support of the WAH and PCR/SCR designated uses for pH at all but one site in the watershed, predicted loads were only calculated for the one non-support segment in Little Cypress Creek (Table 8).

Table 8 Predicted Ion Load for Little Cypress Creek - Site DOW03005007

Site	Cumulative Q (cfs)	Predicted load cumulative (g/day)	Predicted load cumulative (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	1.58	6047.92	13.3332

Load Reduction Allocation

Once a TMDL is developed for a watershed, the needed load reductions can be determined. One way to accomplish this objective is through the use of unit load reductions applied to different land uses within the watershed. The impacts of such reductions in meeting the WQS can then be verified through mathematical simulation. Alternatively, separate TMDLs and associated load reductions can be developed for individual sites within the watershed.

Using the most recent KDOW data, a load reduction was calculated for the pH-impaired segment in Little Cypress Creek by subtracting the TMDL from the predicted load (Table 9). Figure 7 demonstrates this relationship where the existing hydrogen ion loading curve falls well above the TMDL curve.

Load reduction allocations were carried out for the entire watershed using the 2001/2002 Murray monitoring data, this information is also included in Appendix B.

Table 9 TMDL Summary and Reduction Needed

Site	Incremental upstream contributing area (mi2)	Incremental critical flow (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Predicted incremental load (lbs/day)	Load reduction needed (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	2.54	1.58	0.0085	13.3332	13.3247

Permitting

New permits for discharges to streams in the Cypress Creek Watershed could be allowed anywhere with the exception of the watershed area draining to the impaired segment of Little Cypress Creek (Figure 3). New permits in this area could be allowed contingent upon effluent pH permit limits in the range of 6.35 to 9.0 standard units. Kentucky WQS state that the pH value should not be less the 6.0 nor greater than 9.0 for meeting the designated uses of PCR/SCR and WAH. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits. However, because a stream impairment exists (low pH), new discharges cannot cause or contribute to an existing impairment. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2005). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low-pH impairment. Permits having an effluent limit pH of 6.35 to 9.0 standard units will not be assigned a hydrogen ion load as part of a Waste Load

Allocation (WLA). There are currently no active permits in the headwaters of Little Cypress Creek.

Distribution of Load

Because there were no KPDES-permitted (i.e. point source) discharges to the impaired segment during the 2008/2009 study period, the hydrogen ion load for the watershed was defined entirely as a nonpoint source load. Because new permits (pH 6.35 to 9.0) would not cause or contribute to the existing impairment, no load has been provided for the WLA category.

Table 10 Wasteloads and Load Allocations in the Little Cypress Creek Watershed

Site	Incremental critical flow (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation* (lbs/day)	Load Allocation (lbs/day)
Little Cypress Creek 8.7 to 10.1 (DOW03005007)	1.58	0.0085	0.00	0.0085

NOTE: New and current permits will have effluent pH limits in the range of 6.35 to 9.0 standard units

Implementation/Remediation Strategy

Remediation of pH impaired streams as a result of current mining operations is the responsibility of the mine operator. The Kentucky Department for Natural Resources is responsible for enforcing the Surface Mining Control and Reclamation Act of 1977 (SMCRA). The Kentucky Division of Abandoned Mine Lands (DAML) is charged with performing reclamation to address the impacts from pre-law mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of AML problem types.

Practical application of pH TMDLs, especially for AML, will normally involve a phased implementation approach with associated monitoring in order to insure that the implemented measures are having the desired effect. Typical remediation strategies have involved channel restoration, re-vegetation, and the use of agricultural limestone. On sites where applicable (and funding allows) passive treatment systems have been used to treat AMD including open limestone channels, vertical flow systems, limestone dosing, and constructed wetlands.

There are currently no planned remediation activities for the Cypress Creek watershed. However, reclamation activities are underway at other locations within the state where water quality is affected by AMD. From 1985 through 2008, the DAML has spent approximately $24.5 million dollars on various reclamation projects in western Kentucky. Examples of AML projects addressing AMD in western KY are summarized in Table 11.

In 2000, the total federal Kentucky AML budget allocation was approximately $17 million. At the time, the bulk of these funds were used to support Priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and Priority 2 (adverse effects to public health, safety, and welfare) projects. Of the total annual federal budget allocation, AML received only approximately $700,000 in Appalachian Clean Streams Initiative funds, which were targeted for Priority 3 environmental problems.

In June 2003, Clean Water Act Section 319(h) Clean Water Action Plan funds were awarded to the DAML for the Homestead Refuse Reclamation Project that included reclamation of a 92-acre area of the upper Pleasant Run watershed. The total cost of the reclamation project is $1.26 million, with 60% federal funds and 40% state funds. The reclamation activities included channel restoration, re-vegetation, and the use of agricultural limestone.

With the re-authorization of SMCRA in November 2006, the DAML budget was increased to 30 million which included 3.5 million annually set aside for AMD projects during 2007 and 2008.

Table 11 Kentucky Division of Abandoned Mine Lands Reclamation Projects

Watershed	Project Name	Cost
Beech Creek	Bryan/Piper Headwalls	$367,898
Brier Creek	Brier Creek	$522,041
	Buttermilk Road	$403,320
Clear Creek	Eddie Tapp	$100,000
Crab Orchard Creek	Crab Orchard Mine	$1,038,203
	Zugg Borehole	$11,974
Long Falls Creek	Panther Tipple/Panther Pits	*$2,400,442*
Pleasant Run	Pleasant Run	$2,162,085
	Pleasant Run II	$421,384
	Pleasant Run III	$867,477
	Homestead Project	$1,339,260
Pond Creek	Pond Creek I	$50,118
	Pond Creek II	$3,801,740
	Pond Creek III	$4,011,514
	Drakesboro Tipple	$134,371
	Coiltown Mines	$1,350,045
Pond River	Vogue	$308,667
Flat Creek	East Diamond Mine	$535,000
	Flat Creek	$720,572
Flat/Richland Ck	Bunt Sisk Hills	*$974,841*
Render Creek	McHenry Coop. Agreement	$130,165
	McHenry II	$1,075,340
	Vulcan Mine	$585,359
Various Watersheds	Western KY Shafts II	$422,600
Various Watersheds	Western KY Shafts II	*$765,000*
Total		**$24,499,416**

Note: Italicized costs are for projects currently ongoing or in design.

Load Reduction Strategy Using Limestone Sand

Studies in West Virginia (Clayton, et. al., 1998) and Kentucky (Carew, 1998) have demonstrated that limestone sand can be used as an effective agent for restoring the pH in acidified streams. For streams with a pH < 6, $CaCO_3$ may be used to neutralize free hydrogen ions based on the following relationship:

$$CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{2+} \qquad (11)$$

Thus, the theoretical total mass of $CaCO_3$ required to neutralize 1 gm of H^+ ions can be obtained by dividing the molecular weight of $CaCO_3$ (100) by the molecular weight of 2 hydrogen atoms (2) to yield:

$$\text{Required mass of limestone} = 50*\text{Mass of Hydrogen Ions} \qquad (12)$$

Or, in terms of a required annual load:

$$\text{Annual required mass of limestone} = 18{,}250*\text{Mass of Hydrogen Ions (g/day)} \qquad (13)$$

In practice, however, this value will only represent a lower bound of the required mass as a result of two issues: 1) not all the limestone added to a stream will be readily available as soluble $CaCO_3$, and 2) an increasing fraction of the $CaCO_3$ mass will be required to neutralize other metal ions (e.g. Fe, Al, Mn) that will also most likely be present in AMD, especially in the case of streams with pH < 4.5 (Snoeyink and Jenkins, 1980)**.**

One way to deal with the first limitation is to simply add more limestone to the stream. Recent studies in both West Virginia and Kentucky have found that application rates of 2 to 4 times the theoretical limestone requirement have been found to be effective in restoring AMD streams. The most effective way to deal with the second limitation is to determine the additional amount of limestone that must be added to neutralize both the hydrogen ions and the additional ions that might be present. One way to approximate this quantity is by calculating the total acidity in the water column (as expressed directly as $CaCO_3$).

Total acidity is normally defined as a measure of the concentration of acids (both weak and strong) that react with a strong base. Acidity may be determined analytically by titrating a water sample with a standard solution of a strong base (e.g. NaOH) to an electrometrically observed end point pH of 8.3. (For waters associated with AMD it is important that any ferric salts present must first be oxidized prior to the determination of the total acidity). The required mass of NaOH required to raise the sample pH to 8.3 can then be expressed directly in terms of $CaCO_3$ as follows:

$$\text{Acidity, as mg } CaCO_3 = \frac{50{,}000*(\text{mL of NaOH})*(\text{Normality of NaOH})}{\text{Weight of sample used (mg)}} \qquad (14)$$

In general, a relationship between pH (or the associated mass of free hydrogen ions), and the total acidity can be readily developed for a given stream using measured values of pH and acidity (Clayton, et. al, 1998). Using measured streamflow data, an additional relationship between the required hydrogen ion reduction (required to raise the pH up to 8.3) and the corresponding load of $CaCO_3$ (required to neutralize both the hydrogen ions and other free ions) can also be determined such as the one shown in Figure 8. In this particular case, Figure 8 was constructed from an analysis of data from five separate watersheds in the western Kentucky Coal Fields, and thus provides a regional curve for application to similar watersheds in the area. A similar curve could be developed for application to watersheds in other areas using regional data for those areas. Alternatively, a site-specific curve could be developed for an individual watershed using measured values of flow, pH, SC, and total acidity.

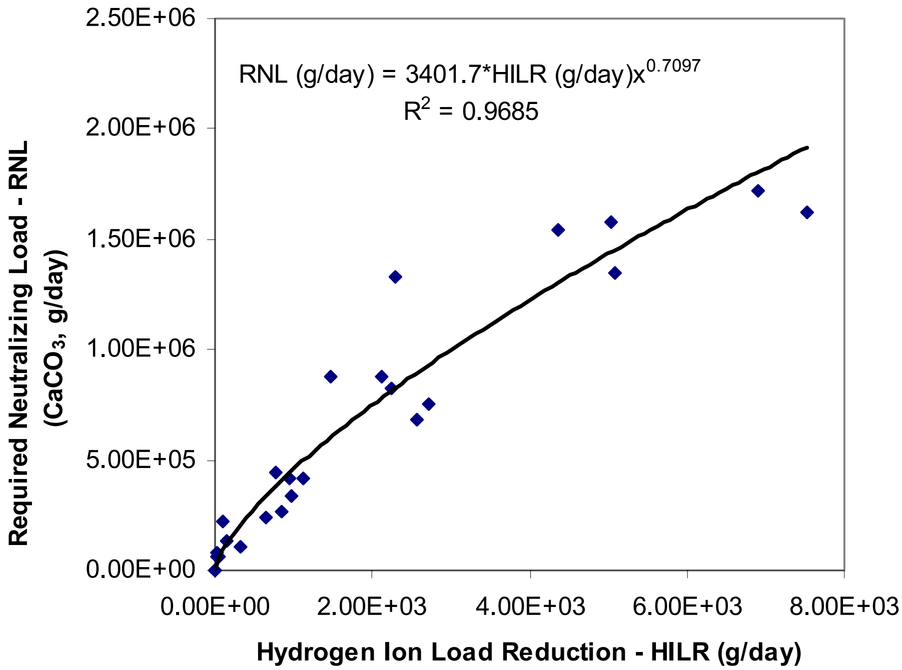


Figure 8 $CaCO_3$ Loading vs Required Hydrogen Ion Reduction

For the case of Cypress Creek, site-specific stream acidity data were not collected as part of the overall sampling effort. As a result, the required $CaCO_3$ loading was determined using the regional curve. It should be recognized that the loading values produced by application of Figure 8 should theoretically increase the pH to 8.3 (based on the definition of total acidity), although pragmatically the achieved value will likely be less. As a result, Figure 8 is likely to provide a conservative estimate of the $CaCO_3$ loading required initially for a particular stream. Subsequent applications of limestone can be further refined through follow-up monitoring.

LITERATURE CITED

Carew, M, (1998*) Rock Creek Reclamation Project, Kentucky Department for Surface Mining Reclamation and Enforcement*, Kentucky Division of Abandoned Mine Lands, 12 pp.

Clayton, J.L., Dannaway, E.S., Menendez, R., Rauch, H.W., Renton, J.J., Sherlock, S.M. and Zurbuch, P.E. (1998). "Application of limestone to restore fish communities in acidified streams". *North American Journal of Fisheries Management*, 18: 347-360.

EPA, (1981) *Clean Water Act*, Section 303(d), 40 CFR Part 130, 1991b.

EPA, (1991) *Technical Support Document for Water Quality-based Toxics Control*, EPA 505/2-90-001, March 1991.

Kentucky Administrative Regulations, (2002) Title 401, Chapters 10:029, 10:031, and 10:040.

Kentucky Division of Water, (1981) *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky*, Department for Environmental Protection, Kentucky Natural Resources and Environmental Protection Cabinet.

Kentucky Division of Water, (proposed 2010) *303(d) Lists of Waters for Kentucky*, Kentucky Department for Environmental Protection, Energy and Environment Cabinet, Division of Water.

Kentucky Division of Water (2005) Personal communications between Mark Carew (Department of Natural Resources) and Andrea Fredenburg (KDOW), April 2005

National Resource Council, (2001) Assessing the TMDL Approach to Water Quality Management, National Academy Press, Washington, D.C.

Snoeyink, V.L., and Jenkins, D., (1980) *Water Chemistry*, Wiley, Inc, New York, NY, 1980, pp. 77-78.

US Department of Agriculture, Soil Survey of Mulenberg County Kentucky, 1977

US Geological Survey, (1983) *Hydrology of Area 34, Eastern Region, Interior Coal Province, Kentucky, Indiana, and Illinois*, Water Resources Investigations Open File Rep. 82-638, Louisville, KY, 42-43

APPENDIX A: MINING PERMITS NUMBERING SYSTEM

XXXX-XX Permit issued prior to May 3, 1978. Ex. 1357-76. The first four numbers represent the mine number. The last two numbers represent the year of issuance.

XXX-XXXX Permit issues after May 3, 1978. The first three numbers indicate the location of the mine by county and the timing of the original permit issuance. (Ex. Hopkins County = 54).

If the first three numbers correspond to the county number, the permit was originally issued during the interim program.

If 200 has been added to the county number, the permit was originally issued prior to May 3, 1978, and carried through into the interim program. Ex. 254 (Hopkins)

If 400 has been added to the county number the permit was issued prior to the Permanent Program and was to remain active after January 18, 1983. Ex. 454 or 654 (Hopkins)

If 800 has been added to the county number: (1) the application is for a permit after January 18, 1983 or (2) two or more previously permitted areas have been combined into a single permit. Ex. 854 (Hopkins)

The last four numbers indicate the type of mining activity being permitted.

COAL

0000-4999	Surface Mining
5000-5999	Underground Mine
6000-6999	Crush/Load Facility
7000-7999	Haul Road Only
8000-8999	Preparation Plant
9000-9399	Refuse Disposal

NON-COAL

9400-9499	Limestone
9500-9599	Clay
9600-9699	Sand/Gravel
9700-9799	Oil Shale
9800-9899	Flourspar

APPENDIX B: 2001/2002 HYDROGEN ION LOADING MODELS

The data selected for model derivation are all of the Murray samples from 2001 except for the highest flow value which is excluded from consideration in order to avoid biasing the model toward the higher flows. The 2001 data represented the worst case of loading. For Sites 2, 3, and 4, the 2/23/02 sample is also included in order to bracket the critical flow value otherwise the critical flow loading would be extrapolated beyond the model's data range. When the 2/23/02 sample is included for Site 2, the result is a hydrogen ion loading line well below the TMDL curve; however, in order to insure a conservative result, in this case the 2001 data is extrapolated to a higher flow. Similar relationships were developed for the other Murray sites and subsequently used to determine incremental loads.

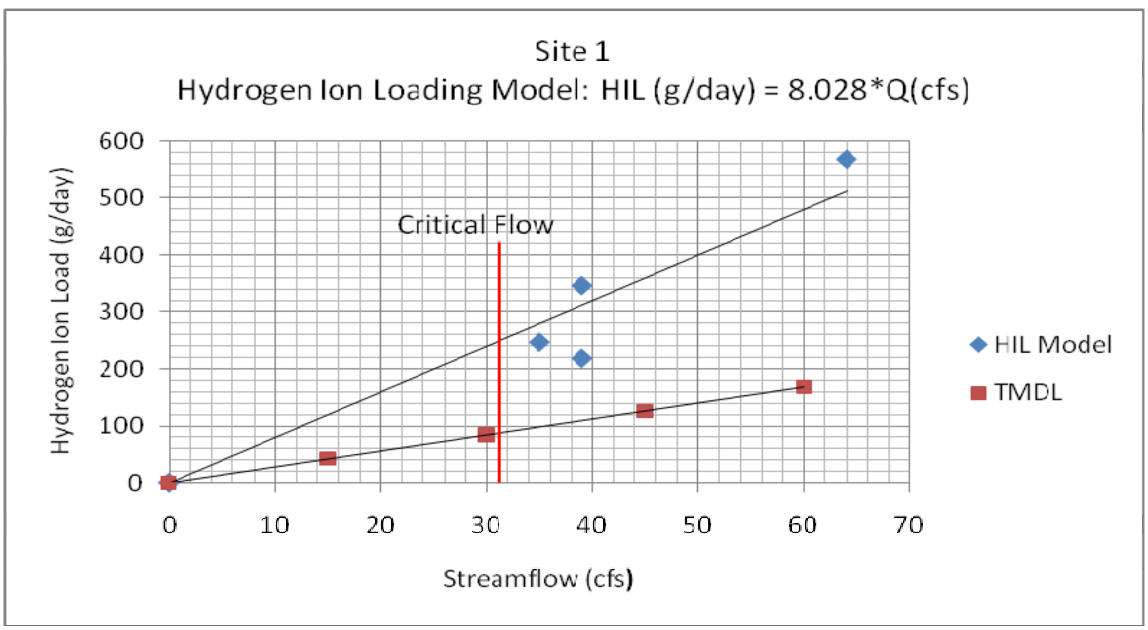
Using the Murray data, incremental loads associated with site 1 were obtained by subtracting the sum of cumulative loads for sites 4, 5 and 8 from the cumulative load for site 1. The incremental load for site 8 can similarly be obtained by subtracting the sum of the cumulative loads for sites 9 and 11 from the cumulative load for site 8. However, the cumulative load for site 4 obtained by its respective hydrogen ion loading model is less than the sum of the cumulative loads for sites 2 and 3 obtained by their respective hydrogen ion loading models. Hence, if the incremental load of site 4 was calculated by subtraction, the value would be negative. The value of the incremental loading for site 4 was therefore set to zero. The numerically consistent option for the cumulative loading of site 4 would be to set it equal to the sum of the cumulative loadings of sites 2 and 3; however, this would not be the most conservative approach to the problem. If a mitigating effect occurred in site 4 which resulted in a lower cumulative loading, then the problem in site 1 may be as large as the modeled numbers suggest; hence, using the lower cumulative loading of 6.72 g/day results in a higher load reduction for site 1 where it may be needed.

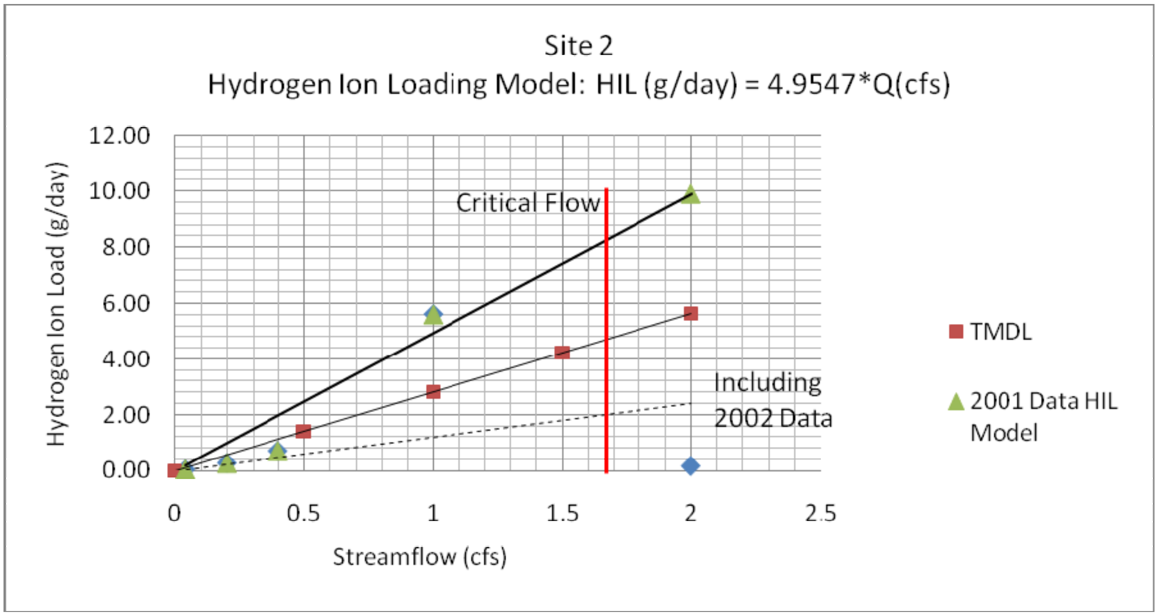
Predicted Loads for the Cypress Creek Watershed Using 2001/2002 Murray Monitoring Data

Site	Cumulative Q (cfs)	Incremental Q (cfs)	Predicted load cumulative (g/day)	Predicted load cumulative (lbs/day)	Predicted load incremental (g/day)	Predicted load incremental (lbs/day)
1	31.42	10.28	252.26	0.5562	242.96	0.5357
2	1.68	1.68	8.31	0.0183	8.31	0.0183
3	6.92	6.92	5.30	0.0117	5.30	0.0117
4	10.77	2.17	3.96	0.0087	0.00	0.0000
5	1.96	1.96	1.39	0.0031	1.39	0.0031
8	8.41	6.80	3.95	0.0087	3.71	0.0082
9	1.06	1.06	0.17	0.0004	0.17	0.0004
11	0.56	0.56	0.07	0.0002	0.07	0.0002

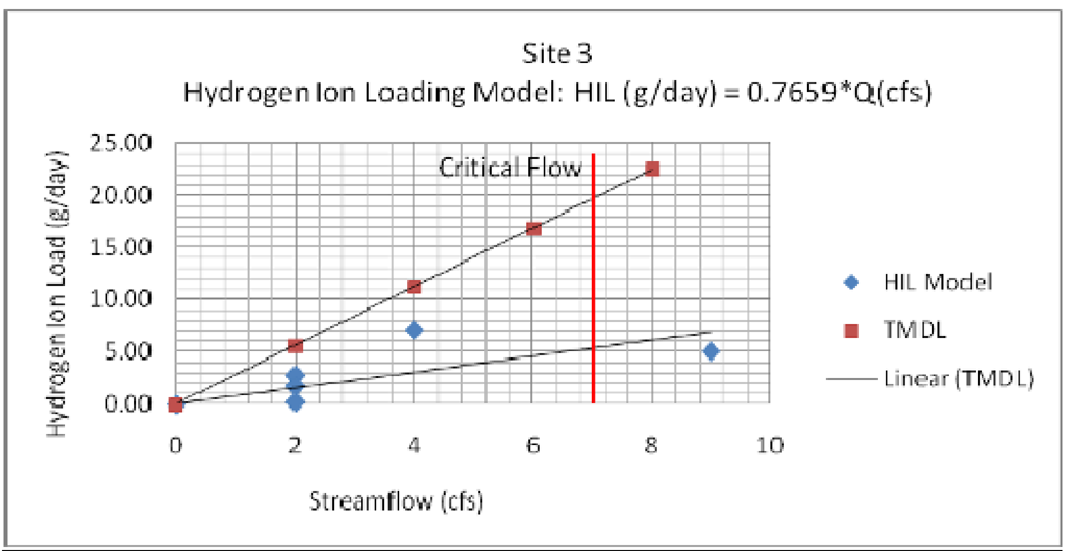
Load Reductions for the Cypress Creek Watershed Using 2001/2002 Murray Monitoring Data

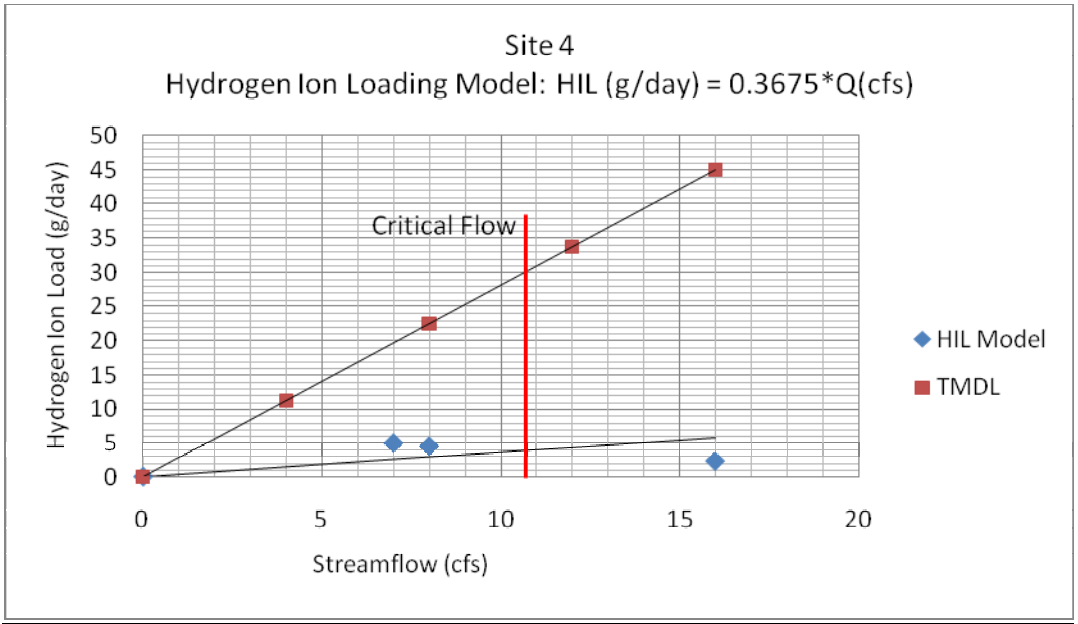
Site	Incremental upstream contributing area (mi2)	Incremental critical flow (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Predicted incremental load (lbs/day)	Load reduction needed (lbs/day)
1	16.55	10.28	0.0555	0.5357	0.4803
2	2.70	1.68	0.0090	0.0183	0.0093
3	11.15	6.92	0.0374	0.0117	0.0000
4	3.50	2.17	0.0117	0.0000	0.0000
5	3.15	1.96	0.0106	0.0031	0.0000
8	10.95	6.80	0.0367	0.0082	0.0000
9	1.70	1.06	0.0057	0.0004	0.0000
11	0.90	0.56	0.0030	0.0002	0.0000

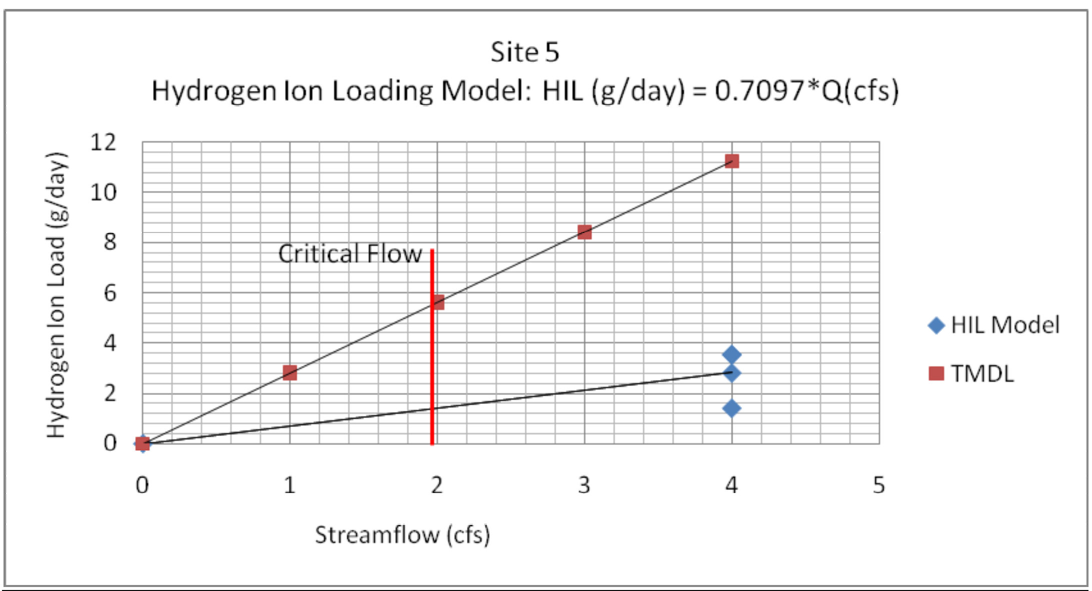


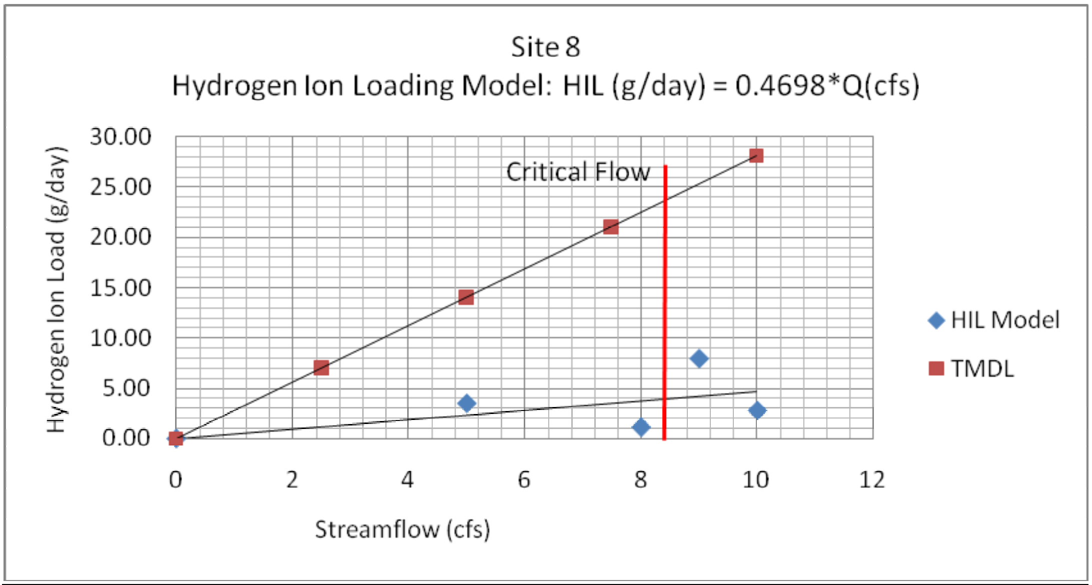


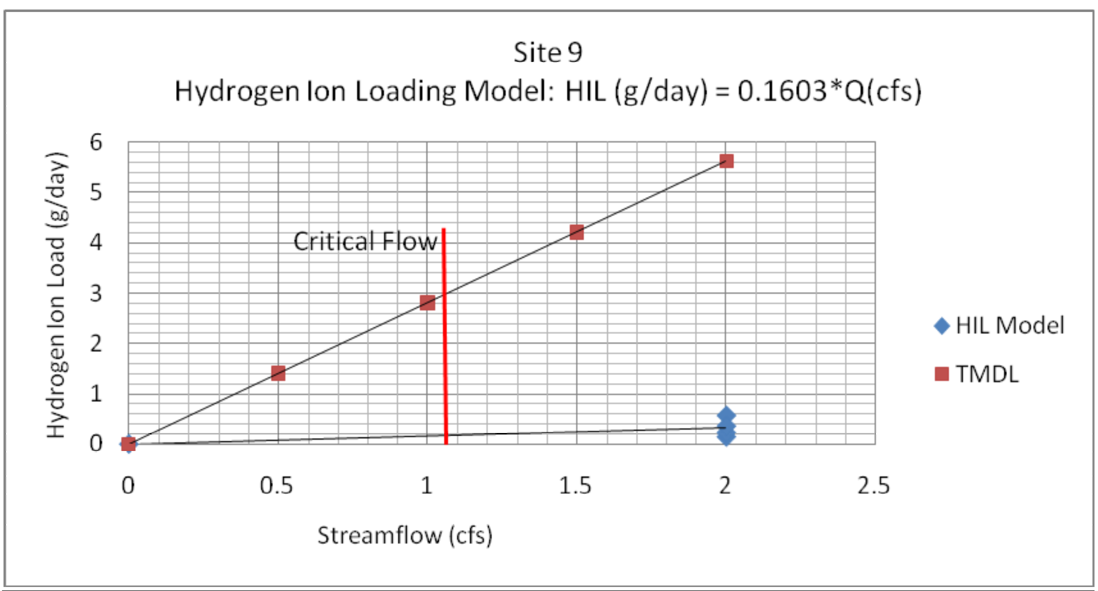
Note for Site 2: the point on the 2001 Data HIL Model corresponding to 2 cfs is not part of the data; it was placed on the actual trend line so that Excel would extend the line for visual reference.

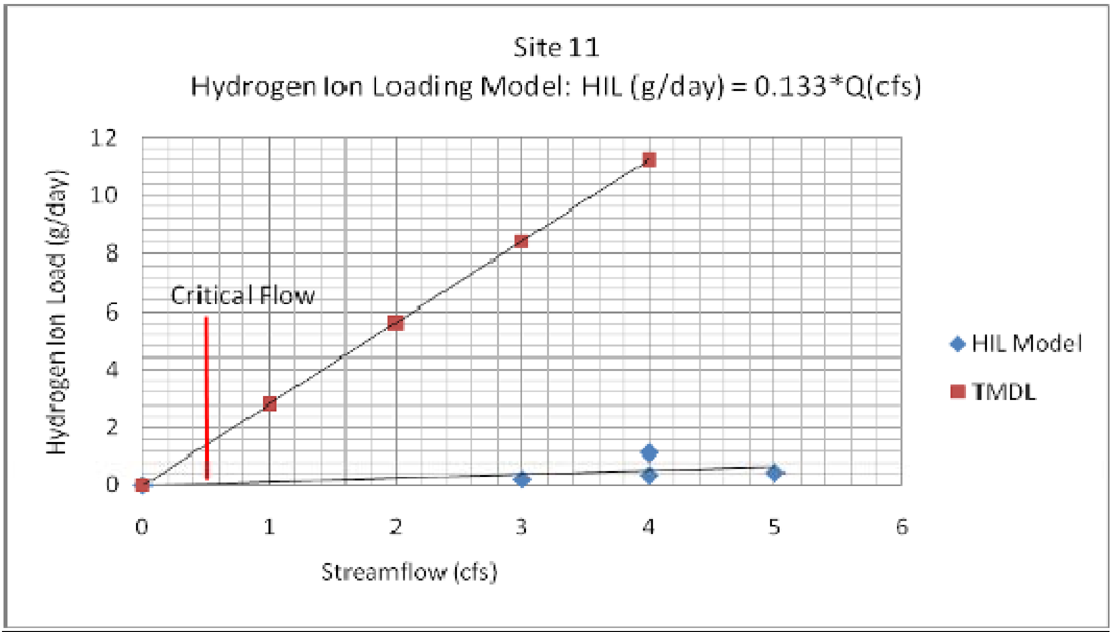



Site 4
Hydrogen Ion Loading Model: HIL (g/day) = 0.3675*Q(cfs)
Hydrogen Ion Load (g/day)
50
45
40
35
30
25
20
15
10
5
0
Critical Flow
0
5
10
15
20
Streamflow (cfs)
HIL Model
TMDL


Site 5
Hydrogen Ion Loading Model: HIL (g/day) = 0.7097*Q(cfs)
Hydrogen Ion Load (g/day)
12
10
8
6
4
2
0
Critical Flow
0
1
2
3
4
5
Streamflow (cfs)
HIL Model
TMDL


Site 8
Hydrogen Ion Loading Model: HIL (g/day) = 0.4698*Q(cfs)
Hydrogen Ion Load (g/day)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0
2
4
6
8
10
12
Streamflow (cfs)
Critical Flow
HIL Model
TMDL


Site 9
Hydrogen Ion Loading Model: HIL (g/day) = 0.1603*Q(cfs)
Hydrogen Ion Load (g/day)
6
5
4
3
2
1
0
0
0.5
1
1.5
2
2.5
Streamflow (cfs)
Critical Flow
HIL Model
TMDL


Site 11
Hydrogen Ion Loading Model: HIL (g/day) = 0.133*Q(cfs)
Hydrogen Ion Load (g/day)
Critical Flow
Streamflow (cfs)
HIL Model
TMDL
0
2
4
6
8
10
12
0
1
2
3
4
5
6